

Fluctuations in Symmetric Diblock Copolymers: Testing A Recent Theory

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Abstract

Composition fluctuations in disordered melts of symmetric diblock copolymers are studied by Monte Carlo simulation over a range of chain lengths and interaction strengths. Results are used to test three theories: (1) the random phase approximation (RPA), (2) the Fredrickson-Helfand (FH) theory, which was designed to describe large fluctuations near an order-disorder transition (ODT), and (3) a more recent renormalized one-loop (ROL) theory, which reduces to FH theory near the ODT, but which is found to be accurate over a much wider range of parameters.

Diblock copolymers are linear polymers that contain two blocks of chemically distinct monomers. Diblock copolymer melts can exhibit both a disordered phase and a variety of periodic ordered phases.¹ Composition fluctuations in the disordered phase can be measured by small angle x-ray and neutron scattering experiments. The structure factor $S(q)$ measured in such experiments is well approximated for very long polymers far from any transition by the random phase approximation² (RPA). The RPA for $S(q)$ is based on the same physical approximations as those underlying the self-consistent field (SCF) theory that is often used to describe the ordered phases. Several closely related coarse-grained theories that attempt to improve upon the RPA^{3–13} yield corrections that decrease with increasing chain length N , and thus reduce to the RPA in the limit $N \rightarrow \infty$. The simulations presented here were designed to test the quantitative accuracy of these theories.

We consider the structure factor $S(q)$ in a dense liquid of symmetric AB diblock copolymers, each of N monomers. Let

$$S(q) \equiv \int d\mathbf{r} \, \mathbf{e}^{i\mathbf{q}\cdot\mathbf{r}} \langle \delta\psi(\mathbf{r}) \delta\psi(0) \rangle, \quad (1)$$

where $\delta\psi(\mathbf{r}) \equiv \delta c_A(\mathbf{r}) - \delta c_B(\mathbf{r})$ and $q \equiv |\mathbf{q}|$. $\delta c_i(\mathbf{r})$ is the deviation of the number concentration $c_i(\mathbf{r})$ of i monomers from its spatial average. In a diblock copolymer melt, $S(q)$ is maximized at a nonzero wavenumber q^* .

The RPA predicts² an inverse correlation function of the form

$$cNS_0^{-1}(q) = F(qR_{g0}) - 2\chi_e N, \quad (2)$$

where $R_{g0} = (N/6)^{1/2}b$ is the radius of gyration of a random walk polymer with statistical segment length b , and c is the total monomer concentration. The parameter χ_e is an effective interaction parameter that is used in the RPA and SCF theories to characterize the degree of incompatibility. Here, $F(x)$ is a known dimensionless function² that has a minimum at a value x^* , yielding a maximum in $S_0(q)$ at a corresponding wavenumber $q_0^* \equiv x^*/R_{g0}$. The subscript of ‘0’ is used to denote RPA predictions for the quantities $S(q)$, R_g and q^* . For symmetric diblock copolymers, $F(x^*) = 21.99$ and $x^* = 1.95$, so that $S_0(q)$ diverges at a predicted spinodal value $(\chi_e N)_s = 10.495$.

A series of closely-related coarse-grained theories have attempted to improve upon the RPA by taking into account fluctuation effects that it neglects.^{3–13} Here, we compare simulation results to the Fredrickson-Helfand³ (FH) theory, which was the first such theory for diblock copolymers, and the renormalized one-loop (ROL) theory,^{10–13} which is the most recent. These theories all yield

predictions for $S^{-1}(q)$ as a sum $S^{-1}(q) = S_0^{-1}(q) + \delta S^{-1}(q)$, in which the correction $\delta S^{-1}(q)$ is proportional to a small parameter $\bar{N}^{-1/2}$ with $\bar{N} \equiv Nb^6c^2$. Physically, $\bar{N}^{1/2} = N^{1/2}b^3c$ is a measure of overlap: It is proportional to the number $\bar{N}^{1/2} \sim R^3/V$ of chains of excluded volume $V = N/c$ that can pack in the volume R^3 pervaded by a chain of size $R \sim \sqrt{\bar{N}}b$.

The FH theory for $S(q)$ was designed to describe the dominant effects of strong composition fluctuations very near the order-disorder transition (ODT) of a melt of long, symmetric diblock copolymers. It yields a simple nonlinear equation for the peak intensity $S(q^*)$. This can also be expressed in terms of an “apparent” interaction parameter χ_a^* that we define by fitting $S(q^*)$ to the RPA, by taking

$$cNS^{-1}(q^*) \equiv 2[(\chi_e N)_s - \chi_a^* N], \quad (3)$$

where $(\chi_e N)_s = 10.495$. The FH theory predicts

$$cN\delta S^{-1}(q) = \bar{N}^{-1/2} \frac{B}{[(\chi_e N)_s - \chi_a^*]^{1/2}}, \quad (4)$$

with $B = 280$.

More recently, several groups have developed a family of renormalized one-loop (ROL) theories of correlations in polymer liquids^{6–13} with a potentially wider range of validity. The characteristic feature of these theories is the development of methods to distinguish non-universal effects of monomer-scale correlations from the universal effects of long-wavelength correlations, and to absorb the effects of short-wavelength correlations into renormalized values of the RPA parameters b and χ_e . Beckrich, Wittmer and colleagues in Strasbourg^{7,8} have developed a theory for universal deviations from random-walk statistics in homopolymer melts, and verified their predictions by extensive simulations. Wang⁶ gave predictions for $S(q)$ near $q = 0$ in homopolymer blends. Our group^{10–14} has developed predictions for $S(q)$ and single-chain correlations in both blends and diblock copolymer melts for arbitrary q , which reduce to the results of other authors in appropriate limits. The ROL theory for symmetric diblock copolymers^{10,12,13} predicts a correction of the form

$$cN\delta S^{-1}(q) = \bar{N}^{-1/2} H(qR_{g0}, \chi_a^* N) \quad , \quad (5)$$

in which the dimensionless function H is defined a sum of Fourier integrals that we evaluate numerically. This expression has been shown^{12,13} to approach the FH prediction of Eq. (4) very near the ODT. This ROL prediction also appears^{10,12} to be the first correction to the RPA within a systematic expansion of $cN\delta S^{-1}(q)$ in powers of $\bar{N}^{-1/2}$. Because the validity of this expansion is

not restricted to the vicinity of the ODT, we expect the ROL theory (but not FH theory) to remain accurate for $\bar{N} \gg 1$ even far from the ODT.

The limitations of the RPA have been well documented by previous simulations of diblock copolymer melts^{15–18} and experiments.^{19–21} Both experiments and simulations show a decrease in q^* with decreasing temperature T and a nonlinear dependence of the peak intensity $S(q^*)$ on $1/T$ near the ODT that are not predicted by the RPA. Previous simulations have not, however, provided very precise tests of the absolute accuracy of the RPA or (particularly) of theories that predict corrections to the RPA. One reason for this has been the absence of a clear prescription for relating the interaction parameter χ_e that is required as an input to these coarse-grained theories to the more microscopic parameters that are controlled in a simulation. The analysis presented here uses several methods to avoid or minimize this ambiguity.

Our simulations use a potential energy similar to that of Grest and coworkers.¹⁷ Non-bonded beads interact via a purely repulsive Lennard-Jones potential, with $u_{ij}(r) = \varepsilon_{ij} [4(r/\sigma)^{-12} - 4(r/\sigma)^{-6} + 1]$ for $r < r_c$, with $r_c = 2^{1/6}\sigma$. Consecutive beads within each chain interact via a harmonic bond potential $\kappa(r - l_0)^2/2$. All simulations discussed here use parameters $\varepsilon_{AA} = \varepsilon_{BB} = kT$, $l_0 = \sigma$, and $\kappa = 400kT\sigma^{-2}$, with a total concentration $c = 0.7\sigma^{-3}$. The magnitude ε_{AB} of the AB repulsion is controlled by a parameter $\alpha = \varepsilon_{AB} - \varepsilon_{AA}$, which indirectly controls χ_e .

We have simulated melts of chains of $N = 16, 32, 64$, and 128 beads in a periodic $L \times L \times L$ cubic box. Two values of L were used for each chain length N , to monitor finite size effects. For each N and L , we conducted parallel replica-exchange MC simulations²² of systems with different values of α at constant T . To sample configurations, we combined a hybrid MD/MC move,²³ in which short constant energy MD simulations are used to generate proposed MC moves, with reptation and double-rebridging²⁴ configuration bias moves.

To test the RPA, FH, and ROL theories, one needs an unambiguous way to determine values for the parameters b and χ_e that these theories require as inputs. Our comparisons with theory all use a value of b defined, as by the Strasbourg group,⁸ as a limit $b^2 \equiv \lim_{N \rightarrow \infty} 6R_g^2(N)/N$. This has been evaluated by numerically extrapolating results for $R_g^2(N)$ for homopolymer melts ($\alpha = 0$) of varying N , giving $b = 1.41\sigma$. This definition of b is required for consistency with the ROL theory, which predicts that random-walk statistics⁷ and the RPA for $S(q)$ ¹⁰ with renormalized values of b and χ_e are exact only in the limit $N \rightarrow \infty$. An analogous procedure for estimating for $\chi_e(\alpha)$, discussed below, is also used in some comparisons.

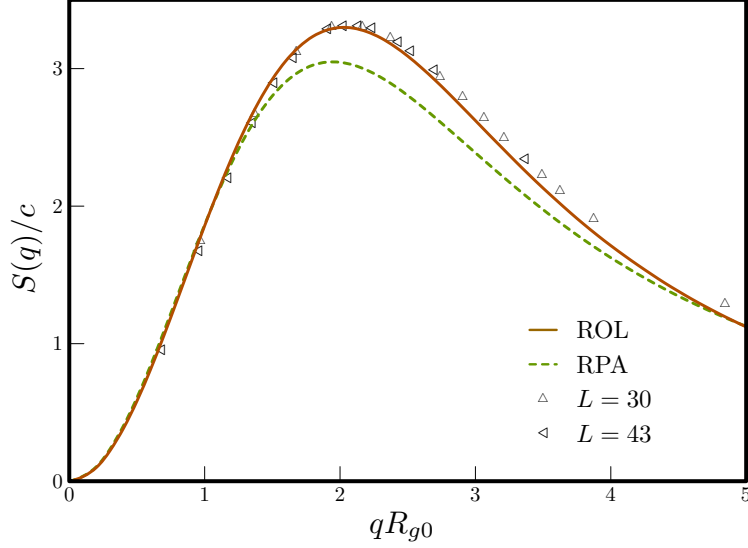


FIG. 1: q dependence of $S(q)$ for $N = 64$, at $\alpha = 0$, for $L = 30$ and $L = 43$. The RPA and ROL predictions are shown by dashed and solid lines, respectively.

Limit $\chi_e = 0$: We first consider the special case of a system with $\alpha = 0$, or $\epsilon_{AB} = \epsilon_{AA}$, corresponding to $\chi_e = 0$. This is an idealization of a neutron scattering experiment in which A and B blocks are labelled by differential deuteration, but are otherwise identical. In this limit, both the RPA and ROL predictions for $S(q)$ depend only on intramolecular correlation functions for chains in a dense melt. The RPA, which assumes random walk statistics, predicts $cN S_0^{-1}(q) = F(qR_{g0})$. The ROL theory yields predictions that differ from the RPA only as a result of predicted $\mathcal{O}(\bar{N}^{-1/2})$ deviations from random walk statistics.¹³

Fig. 1 shows simulation results and predictions for $S(q)$ vs. qR_{g0} in systems with $N = 64$ ($\bar{N} = 240$) and $\alpha = 0$. Here, $R_{g0}^2 \equiv Nb^2/6$, with $b = 1.41\sigma$. Equivalent results are obtained for box sizes $L = 30$ and $L = 43$. The RPA (dashed line) slightly underestimates both the peak amplitude $S(q^*)$ and peak wavenumber q^* . The ROL prediction (solid line), however, fits the data almost perfectly, with no adjustable parameters. We find a similar level of agreement at $\alpha = 0$ for other chain lengths.

Peak wavenumber: We next discuss the evolution of peak wavenumber q^* with changes in α , or $\chi_e(\alpha)$. Fig. 2 shows our results for q^*/q_0^* , where $q_0^* = 1.95/R_{g0}$ is the RPA prediction. The ratio q^*/q_0^* is plotted vs. the quantity $\chi_a^* N$ that is defined in Eq. (3) by fitting the observed peak intensity to the RPA. This plot thus shows peak wavenumber plotted vs. a measure of peak intensity.

Both q^* and $S(q^*)$ were determined by fitting values of $S(q)$ at a discrete set of allowed

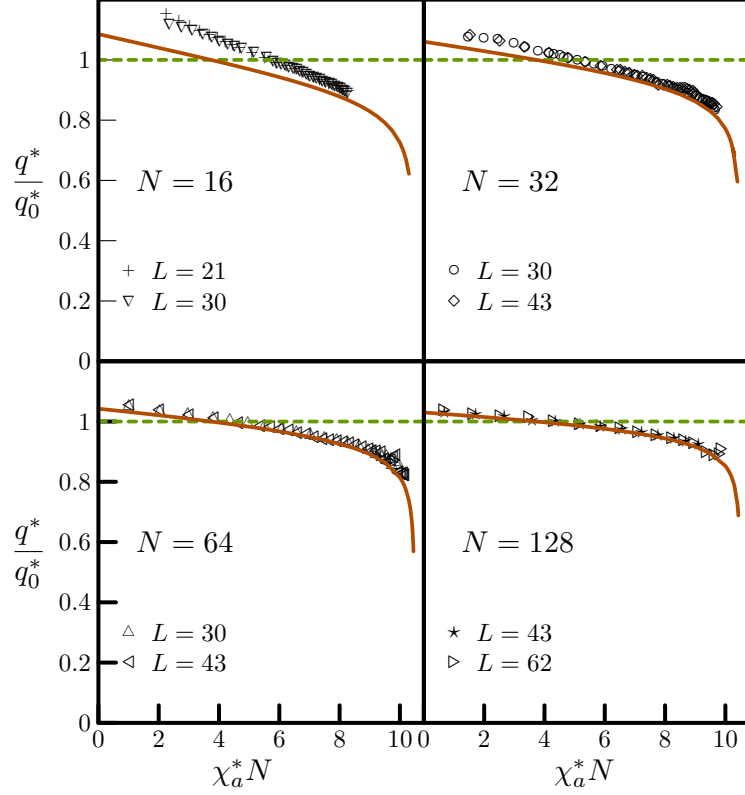


FIG. 2: Peak wavenumber q^* , normalized by the RPA prediction q_0^* , vs $\chi_a^* N$ for $N = 16, 32, 64$, and 128 . Data for two values of box size L are shown for each chain length N . ROL predictions are solid lines.

wavevectors to a smooth function. For $N = 64$ and 128 and large values of α , this procedure becomes unreliable because there are too few allowed values of q within the peak. In Figs. 2 and 3, we thus show results for q^* and $S(q^*)$ for each N and L only over the range of values of α for which the peak remains broad enough to allow a reliable fit. Within these regions, results from different box sizes are consistent, and we see no evidence of a transition to an ordered phase.

Simulation results for q^* decrease monotonically with increasing χ_a^* or α , exhibiting a total drop of 15-20 % over the range shown, in agreement with previous results.¹⁸ Note that $q^*/q_0^* > 1$ for small $\chi_a^* N$, consistent with the behavior shown in Fig. 1 for $\alpha = 0$, and that $q^*/q_0^* < 1$ only for $\chi_a^* N \gtrsim 5$. The RPA predicts a constant $q^*/q_0^* = 1$ (dashed line). ROL predictions (solid lines) were obtained from parametric plots of predictions for q^* and $S(q^*)$ over a range of values of $\chi_e N$. The ROL theory captures all of the observed qualitative features, and is strikingly accurate for the longest chains ($N = 64$ and 128). The predictions appear to become systematically more accurate with increasing N , consistent with the claim^{10,11} that the ROL theory is the first correction to the RPA within an expansion in powers of $\bar{N}^{-1/2}$.

Estimating $\chi_e(\alpha)$: In all of the theories considered here, the degree of incompatibility between A and B monomers is characterized by an effective interaction parameter χ_e . To test the predictions of these theories for how the peak intensity $S(q^*)$ evolves with increasing χ_e , we need an independent estimate of how $\chi_e(\alpha)$ depends on α . (The comparisons shown in Figs. 1 and 2 did not require this.)

We estimate $\chi_e(\alpha)$ using a method based on thermodynamic perturbation theory. Ref.¹⁴ discusses a perturbation theory for a structurally symmetric blend of A and B homopolymers, both of length N , with a pair potential $u_{ij}(r) = \epsilon_{ij}u(r)$, with $\epsilon_{AA} = \epsilon_{BB}$ and $\alpha = \epsilon_{AB} - \epsilon_{BB}$, in which the excess free energy per monomer $f_{ex}(\alpha, N)$ is expanded in powers of α . In such a model, $f_{ex}(\alpha = 0, N) = 0$. It was shown¹⁴ that f_{ex} is given to $\mathcal{O}(\alpha)$ by $f_{ex}(\alpha, N) \simeq \alpha z(N) \phi_A \phi_B$, where ϕ_i is the fraction of i monomers, and where

$$z(N) = \int d\mathbf{r} g(\mathbf{r}; N) u(\mathbf{r}). \quad (6)$$

Here, $g(\mathbf{r}; N)$ is the inter-molecular radial distribution function in the reference state with $\alpha = 0$. By comparing this perturbation theory to ROL predictions for $S(q)$ at $q = 0$, which reduce to the RPA in the limit $N \rightarrow \infty$, while also expanding $\chi_e(\alpha)$ in powers of α , it was found that the RPA parameter χ_e is given to $\mathcal{O}(\alpha)$ by

$$\chi_e \simeq z(\infty) \alpha / kT, \quad (7)$$

where $z(\infty) \equiv \lim_{N \rightarrow \infty} z(N)$. For the model considered here,¹⁴ we find $z(\infty) = 0.2965$. Perturbation theory provides a useful description of the homogeneous state of both blends and diblock copolymer melts because the critical values of α and χ_e are proportional to $1/N$, implying that the accuracy of perturbation theory must improve with increasing N .

Peak intensity: Fig. 3 shows how the inverse peak intensity $cNS^{-1}(q^*)$ varies with $\chi_e N$, plotted using Eq. (7) for $\chi_e(\alpha)$. Fig. 3(a) compares results for chains with $N = 64$ to the RPA (straight dashed line), FH (dot-dashed), and ROL (solid) predictions. Fig. 3(b) compares results for chains of length $N = 32, 64$, and 128 to RPA and ROL predictions. The comparisons to theory involve no adjustable parameters.

Several qualitative features are immediately apparent: The quantity $cNS^{-1}(q^*)$ is greater than the RPA prediction (suppressed fluctuations) for $\chi_e N \gtrsim 6$, as predicted by the FH theory, but is less than the RPA prediction (enhanced fluctuations) for $\chi_e N \lesssim 6$. For $\chi_e N \lesssim 10$, results for different N converge towards the RPA prediction with increasing N , as predicted by both FH and ROL theories. In Fig. 3(a), the FH and ROL predictions for $N = 64$ are very similar to

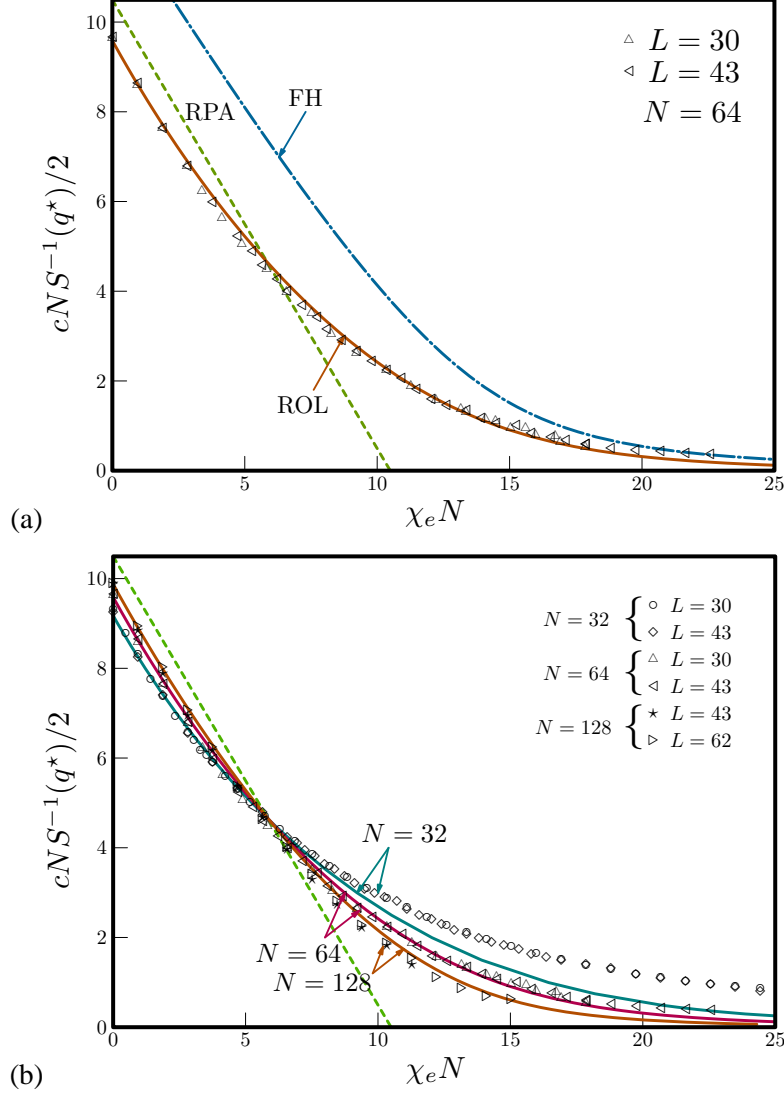


FIG. 3: Inverse peak intensity vs. $\chi_e N$ for $N = 64$ (panel a, upper) and for $N = 32, 64$, and 128 (panel b, lower). For each N , results are shown for two values of the box size L . χ_e is estimated using Eq. (7), using $z_c = 0.2965$. Straight dashed lines show the RPA prediction. Solid lines are ROL predictions. The dot-dashed curve in panel a is the FH prediction.

each other and to the simulation results in the strong fluctuation regime, where $\chi_e N \gtrsim 15$ and $cNS^{-1}(q^*) \lesssim 1$. This is the regime that the FH theory was designed to describe. For $\chi_e N \lesssim 15$, however, the FH theory fails, while the ROL theory remains remarkably accurate, for this chain length, down to $\chi_e N = 0$. The ROL theory correctly predicts a change in the sign of the deviation of $cNS^{-1}(q^*)$ from the RPA prediction at a value of $\chi_e N \simeq 6$, which is shown in Fig. 3(b) to be almost independent of N . The FH theory incorrectly predicts a rather large positive deviation for

all $\chi_e N \geq 0$. In 3(b), the ROL theory is seen to be quite accurate for all three values of N for $\chi_a^* N \lesssim 7$, and to remain accurate for larger values $\chi_e N$ for $N = 64$ and 128 . ROL predictions differ significantly from the results only for the shortest chains shown, with $N = 32$, at large values of $\chi_e N$. Results for $N = 16$ are not shown, but exhibit the same trends, and differ even more from the ROL prediction. The apparent tendency of the ROL theory to become more accurate with increasing N is consistent with the claim that it is part of a systematic expansion in powers of $\bar{N}^{-1/2}$.

The comparison shown in Fig. 3 is subject to at least two types of error: (i) Errors in the ROL theory itself, due to truncation of the loop expansion at first order in $\bar{N}^{-1/2}$, and (ii) Errors in our estimate of χ_e , due to the truncation of the Taylor expansion of $\chi_e(\alpha)$ at first order in α . The comparisons shown in Figs. 1 and 2 are subject only to type (i). The error in $\chi_e(\alpha)$ is expected to depend only on α , and to increase with α . It should be most serious for large values of $\chi_e N$ and small N , because the value of α required to obtain a specified value of $\chi_e N$ increases with decreasing N . The fact that the largest discrepancies between the ROL theory and the simulation results occurs in Fig. 3 for the shortest chains at large values of $\chi_e N$ suggests that our use of a simple linear approximation for $\chi_e(\alpha)$ may be a significant source of error for the shortest chains.

In summary, we have presented an unusually systematic simulation study of how $S(q)$ depends upon both chain length and degree of AB repulsion in AB diblock copolymer melts, and compared our results to several theories. The use of theoretically motivated procedures for obtaining independent estimates of the RPA parameters b and χ_e , defined by extrapolation to $N = \infty$, allowed much more precise comparisons to theory than has previously been possible. The range of values of \bar{N} studied here, $\bar{N} \leq 480$, overlaps the lower end of the range studied in experiments on polymers, for which \bar{N} is more often $10^3 - 10^4$. A recent theory, the ROL theory, is shown to be a substantial improvement over the FH theory, with a much wider range of validity. The ROL theory is strikingly accurate for the longest chain lengths studied, and for sufficiently small values of $\chi_e N$. All our results appear to be consistent with the claim that this theory is the first correction to the RPA within a systematic expansion, and should thus become more accurate with increasing \bar{N} . The results indicate that theories developed to describe subtle deviations from the random-walk and RPA theories in liquids of very long polymers, based on an expansion in powers of $\bar{N}^{-1/2}$, can accurately describe liquids of surprisingly short chains.

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1. F. S. Bates and G. H. Fredrickson, *Physics Today* **52**, 32 (1999).
 2. L. Leibler, *Macromolecules* **13**, 1602 (1980).
 3. G. H. Fredrickson and E. Helfand, *J. Chem. Phys.* **87**, 697 (1987).
 4. J.-L. Barrat and G. H. Fredrickson, *J. Chem. Phys.* **95**, 1281 (1991).
 5. R. Holyst and A. Vilgis, *J. Chem. Phys.* **99**, 4835 (1993).
 6. Z.-G. Wang, *J. Chem. Phys.* **117**, 481 (2002).
 7. P. Beckrich, A. Johner, A. N. Semenov, S. P. Obukhov, H. Benoît, and J. P. Wittmer, *Macromolecules* **40**, 3805 (2007).
 8. J. P. Wittmer, P. Beckrich, H. Meyer, A. Cavallo, A. Johner, and J. Baschnager, *Phys. Rev. E* **76**, 011803 (2007).
 9. D. C. Morse, *Annals of Physics* **321**, 2318 (2006).
 10. P. Grzywacz, J. Qin, and D. C. Morse, *Phys. Rev. E* **76**, 061802 (2007).
 11. J. Qin and D. C. Morse, *J. Chem. Phys.* **130**, 224902 (2009).
 12. D. C. Morse and J. Qin, *J. Chem. Phys.* **134**, 084902 (2011).
 13. J. Qin, P. Grzywacz, and D. C. Morse (2011), arXiv:1105.2241v1 [cond-mat.soft], submitted to JCP.
 14. D. C. Morse and J. K. Chung, *J. Chem. Phys.* **130**, 224901 (2009).
 15. H. Fried and K. Binder, *J. Chem. Phys.* **94**, 8349 (1991).
 16. R. G. Larson, *J. Phys. II France* **6**, 1441 (1996).
 17. M. Murat, G. S. Grest, and K. Kremer, *Macromolecules* **32**, 595 (1999).
 18. M. W. Matsen, G. H. Griffiths, R. A. Wickham, and O. N. Vassiliev, *J. Chem. Phys.* **124**, 024904 (2006).
 19. F. S. Bates, J. H. Rosedale, and G. H. Fredrickson, *J. Chem. Phys.* **92**, 6255 (1990).
 20. K. Almdal, F. S. Bates, and K. Mortensen, *J. Chem. Phys.* **96**, 9122 (1992).
 21. J. H. Rosedale, F. S. Bates, K. Almdal, K. Mortensen, and G. D. Wignall, *Macromolecules* **28**, 1429 (1995).
 22. D. J. Earl and M. W. Deem, *Phys. Chem. Chem. Phys.* **7**, 3910 (2005).
 23. B. Mehlig, D. W. Heermann, and B. M. Forrest, *Phys. Rev. B* **45**, 679 (1992).
 24. B. Banaszak and J. J. de Pablo, *J. Chem. Phys.* **119**, 2456 (2003).